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(57) Abstract A unit that uses carbon and oxygen as fuel sources. In particular, the unit comprises a carbon-containing anode (16), an electrolyte (18) and a solid state cathode (20). Heating the unit to temperatures of 400 °C – 2000 °C provides an electrical output of at least 1 mW.cm ⁻² . A method for generating electricity with a unit comprising a carbon-containing anode, an electrolyte and a solid state cathode.			

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A CARBON-OXYGEN ELECTRICITY-GENERATING UNIT

Field of the Invention

The present invention relates to electricity-generating units or generators such as fuel cells or batteries that use carbon as an electrode. In particular, the invention involves units comprising a carbon-containing anode, an electrolyte and a solid state cathode. The present invention also involves a method for generating electricity with a unit comprising a carbon-containing anode, an electrolyte and a solid state cathode.

Background of the Invention

Fuel cells are arrangements that convert fuel into electricity via chemical reaction. The most common commercially available fuel cells use hydrogen and oxygen as fuel gases. Disadvantages of most current systems include the lack of a readily available hydrogen source, the bulky apparatus needed to contain hydrogen, and the need for safety precautions for storing an explosive gas such as hydrogen. Such disadvantages can lead to increased costs and can preclude or make difficult the development of some compact, portable and mobile applications.

Using carbon as an electrode and/or fuel for an electricity-generating unit presents some unique characteristics over current metal/air, dry cell and wet cell batteries and fuel cells. The ratios of valence number to molecular weight for carbon, 4:12 and 2:12, are high, providing a potential of producing more electrons per unit atomic weight. Hydrogen is the only element that is more efficient than carbon. Unlike hydrogen, conductive carbon sources, such as coal, are abundant and relatively inexpensive. Carbon materials can be fashioned in a variety of shapes that allow for compact designs for mobile applications. Finally, carbon presents minimal safety hazards. Carbon, however is chemically inert under moderate conditions and must be heated to temperatures of at least 400 °C to overcome the activation energy in a reaction with oxygen. For example, coal and graphite react with air rapidly at 750°C and 850 °C respectively.

Patents that disclose the use of carbon as an anode in fuel cells include U.S. Patent Nos. 460,122 and 5,589,289. U.S. Patent No. 460,122 relates to a process for generating electricity by heating carbon or carbonaceous materials to high temperature in the presence of an active agent such as a metal oxide or a salt. The carbon and active agent is contained in

metal pot which also functions as a cathode. The patent suggests that heating the pot results in a reaction between the oxide and carbon to form carbon monoxide and a resulting electrical current. U.S. patent No. 5,589,289 relates to a process for synthesizing a carbon anode. An aromatic organic monomer is subjected to condensation and reduction reactions at high 5 temperature to yield an amorphous carbon material that displays charge and discharge characteristics. The carbon anode has applications for a rechargeable electrochemical cell.

There remains a need to develop more energy efficient electricity generating units that provide a greater electrical output over known products, allow a more compact design for greater mobility, are easy to construct and are safe to use. Accordingly, an object of the 10 present invention is the provision of an electricity generating unit that exhibit improvements such as these. A method and apparatus for generating electricity with a carbon-anode-based unit are also disclosed.

Summary of the Invention

15 The present invention relates to an electricity generating unit with a carbon and oxygen fuel sources for generating electricity and a method for generating electricity with this unit.

One aspect of the invention provides a unit for generating electricity using carbon and 20 oxygen as fuel sources. The unit comprises a carbon-containing anode, an electrolyte in contact with the anode at a first contact surface area and a solid state cathode in contact with the electrolyte at a second contact surface area. The cathode reduces oxygen, O₂, to oxygen anions, O²⁻, and the electrolyte allows passage of oxygen anions to the anode. The unit is operable at a temperature of between 400 °C and 2000 °C and generates an electrical output of at least 1 mW·cm⁻² of the second contact surface area.

25 Another aspect of the invention provides a unit comprising a carbon-containing anode, an electrolyte in contact with the anode at a first contact surface area and a solid state cathode in contact with the electrolyte at a second contact surface area. The unit is constructed and arranged to be continuously operable for at least about 10 hours.

The carbon-containing anode used preferably has a resistivity of between about 10⁻⁵ 30 ohm-cm and about 100 ohm-cm. The anode is solid or in particle form and is preferably selected from the group consisting of graphite, quasi-graphite, coal, coke, charcoal, fullerene, buckminsterfullerene, carbon black, activated carbon, decolorizing carbon and mixtures

thereof.

The invention preferably provides a solid state electrolyte having a dimension therethrough from a first contact surface area adjacent to an anode to a second contact surface area adjacent to a cathode of between about 1 μm and 1000 μm , preferably between about 1 μm and 600 μm and more preferably between about 1 μm and 100 μm . Where the electrolyte is a solid layer, the dimension is preferably between about 1 μm and about 1000 μm , preferably between about 1 μm and 600 μm and more preferably between about 1 μm and 100 μm . The electrolyte most preferably has a formula $(\text{ZrO}_2)_b(\text{HfO}_2)_a(\text{M}'_u\text{O}_v)_c(\text{Y}_2\text{O}_3)_d(\text{M}''_x\text{O}_y)_e$ where a is from 0 to about 0.2, b is from 0 to about 1.0, c is from 0 to about 1.0, d is from 0 to about 0.5, e is from 0 to about 0.15 and at least one of a, b, c, d and e is greater than zero, u is from about 0.2 to about 2.0, v is from about 0.2 to about 2.0, x is an integer greater than 0 and less than or equal to 2, y is an integer greater than 0 and less than or equal to 3, and M (i.e., M' or M'') is selected from the group consisting of manganese, iron, cobalt, nickel, copper, zinc, calcium, cerium, gadolinium, bismuth, samarium, tungsten and thorium.

In one embodiment, the electrolyte has a melting temperature of between about 300 $^{\circ}\text{C}$ and 2000 $^{\circ}\text{C}$. Thus, in this embodiment, the electrolyte can be a molten electrolyte under the operating conditions of the unit. The electrolyte can be selected from the group consisting of a metal carbonate, a metal oxide, a plurality of metal carbonates, a plurality of metal oxides and mixtures thereof.

The solid state cathode of this invention preferably has an oxygen ionization rate of between about 10^{-8} $\text{g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ and about 10^{-3} $\text{g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$. The cathode also has an electrical resistivity of between about 10⁹ ohm-cm to about 100 ohm-cm. The cathode is preferably selected from the group consisting of a metal, a metal oxide, a plurality of metal oxides and mixtures thereof. The solid state cathode preferably has a formula $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_b\text{C}_c\text{O}_d$ where A is an alkaline earth metal, B is selected from the group consisting of scandium, yttrium and a lanthanide metal (e.g., cerium, samarium, gadolinium, erbium), C is selected from the group consisting of titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, bismuth, hafnium, aluminum and antimony, x is from 0 to about 1.05, y is from 0 to about 1, z is from 0 to about 0.5, b is from 0 to about 0.5, c is from 0 to about 0.5 and d is between about 1 and about 5 so that an oxide is always present, and at least one of x, y, z, b and c is greater than zero. The solid state cathode may also have a formula $\text{Li}_x\text{M}_{1-x}\text{O}$ where M is a metal selected from the group consisting of nickel and cobalt and x is from 0 to about 0.25.

In another aspect of the invention, a method is provided for generating electricity in a unit having a carbon-containing anode. The method comprises the steps of providing a carbon-containing anode, an electrolyte in contact with the carbon-containing anode at a first contact surface area and a solid state cathode in contact with the electrolyte at a second contact surface area. An oxygen-containing gas flow is directed to the cathode and the unit is heated to a temperature of between about 400 °C and about 2000 °C to produce an electrical output of at least about 1 mW·cm⁻² of the second contact surface area.

Other advantages, novel features, and objects of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings, which are schematic and which are not intended to be drawn to scale. In the figures, each identical or nearly identical component that is illustrated in various figures is represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

Brief Description of the Drawings

- Fig. 1 shows a semidiagrammatic, cross-sectional view of an embodiment of an electricity generating unit having a solid state electrolyte;
- Fig. 2 shows a top, front perspective view of an embodiment of a solid state electrolyte and a solid state cathode in a flat or planar arrangement;
- Fig. 3 shows a top, front perspective view of an embodiment of a solid state electrolyte and a solid state cathode in a tubular arrangement;
- Fig. 4 shows a top, front perspective view of an embodiment of a solid state electrolyte and a solid state cathode with a supporting substrate in a flat or planar arrangement;
- Fig. 5 shows a top, front perspective view of an embodiment of a solid state electrolyte and a solid state cathode with a supporting substrate in a tubular arrangement;
- Fig. 6 shows a semidiagrammatic, cross-sectional view of an embodiment of an electricity generating unit having a molten electrolyte; and
- Fig. 7 shows a semidiagrammatic, cross-sectional view of an embodiment of an electricity generating unit.

Detailed Description

Fig. 1 shows a semidiagrammatic, cross-sectional view of an embodiment of an electricity-generating unit 10 of the invention. Unit 10 comprises an anodic section 12 and a cathodic section 14. An electrolyte 18 contacts both the anodic section 12 and the cathodic section 14. The anodic section 12 contains a carbon-containing anode 16 at one end, springs 32 and 33, a metal wire lead 34 connected to spring 32 and an inert gas flow from a gas pipe 30. The anode 16, coil springs 32 and 33 and inert gas flow from gas pipe 30 are enclosed within a cylindrical anodic casing 26 and a cap 31. The cathodic section 14 contains a cylindrical planar disk cathode 20 at one end, a metal wire lead 36 connected to the cathode 20 and a source of an oxygen-containing gas for exposure to the cathode, specifically, a flow of an oxygen-containing gas from gas pipe 38 directed towards the cathode 20. Cathode 20, metal wire lead 36 and oxygen-containing gas flow pipe 38 are enclosed within a cylindrical cathodic casing 28. The electricity generating unit 10 can be any source of electricity that uses a carbon-containing electrode, such as a fuel cell where carbon is a fuel source, or a battery such as a high power density battery.

The anodic casing 26 shown in Fig. 1 is cylindrical having a longitudinal axis and a circular base. The base, however can have any closed shape such as a square, rectangular or oval. The anode 16 lies at one end of the anodic casing 26 and the anodic casing 26 is structured for positioning the anode 16 in contact with the electrolyte 18 at a first contact surface area 22. Preferably the anodic casing 26 has a similar base shape and base dimension to facilitate connection of the anodic section 12 with the electrolyte through gold gaskets 27. The material for the anodic casing 26 is preferably alumina although other cylindrical inert temperature-resistant materials can be used.

The carbon-containing anode 16 can be a solid or in particulate form. When the anode 16 is in particulate form, a casing also serves to compact the particulate matter against the electrolyte 18 at the first contact surface area 22, increasing the first contact surface area 22. Accordingly, power output increases with an increase in the first contact surface area 22 between anode 16 and electrolyte 18. In one embodiment, the unit is capable of a voltage of at least about 0.1 volts (V), more preferably at least about 0.5 V, and even more preferably at least about 1.0 V. This increase in first contact surface area 22 may be aided with an urging device to increase the first contact surface 22, such as spring 32 in the embodiment of Fig. 1. Other urging devices include a mechanical device, an electromagnetic device, an electrical

device, a centrifugal device, a gravitational device and a hydraulic and pneumatic device. Examples of urging devices include a clamp, a spring, a stepping motor, a relay and a magnet. Spring 32 is situated within the anodic casing 26 and is aligned parallel to the longitudinal axis. At one end of spring 32 is a flat surface 35 (area of 0.3 cm² in one embodiment) perpendicular to the longitudinal axis which contacts the particulate anode 16. Preferably the spring 32 has a force constant of at least 1 psi. A metal wire lead 34 may be connected to spring 32. In this case, spring 32 preferably has a resistivity at least equal to that of the anode. When the anode is a solid such as a solid block or several solid blocks, the metal wire lead 34 may be connected to the anode directly. Cap 31 is held in a fixed position, and another spring 10 33, positioned under cap 31, keeps a tight seal around the gold gasket or ceramic adhesive (alumina and zirconia) 27, the casing 26, which also has a fixed position, and the electrolyte 15 18.

The carbon-containing anode 16 is a conductive carbon having a resistivity of from about 10⁻⁵ ohm-cm to about 100 ohm-cm; preferably the resistivity is from about 10⁻³ ohm-cm 15 to about 10⁻¹ ohm-cm. The carbon-containing anode may be selected from the group consisting of graphite, quasi-graphite, coal, coke, charcoal, fullerene, buckminsterfullerene, carbon black, activated carbon, decolorizing carbon, and mixtures thereof. Quasi-graphite is a particulate carbon in which the carbon-carbon bonds, having lengths ranging from 1.33 Å to 1.40 Å, are slightly longer than carbon-carbon bonds in graphite which have a length of 1.32 20 Å. Carbon black includes several forms of artificially prepared carbon or charcoal. Examples include animal charcoal obtained by charring bones, meat and blood; gas black, furnace black, channel black and conductive black, obtained by incomplete combustion of natural gas, acetylene gas, oils and other hydrocarbons; lamp black obtained by burning various fats, oils and resins, and activated charcoal such as CarbomixPenn, Carboraffin, MedicoalLundbeck, 25 and Norit, and other carbons, prepared from wood and other natural biomass; and glassy carbon. One particular example is electrically conductive carbon black, obtained as Black Pearl manufactured by Cabot Corp., Boston, MA.

Also included within the anodic section 12 is an inert gas provided through a gas pipe 30 which functions to isolate the anode from the surrounding environment. Because the 30 electricity-generating unit 10 is designed to operate at a temperature of at least about 400 °C, exposing a hot, carbon surface to air in the environment may result in oxidation of the anode, which consequently wastes fuel. In Fig. 1, the inert gas flow pipe 30 is directed towards the

anode and the inert gas may be selected from the group consisting of nitrogen, helium, argon, neon, krypton, nitrogen oxides, sulfur oxides, water vapor, exhaust gases formed during operation of the unit such as carbon dioxide and carbon monoxide, and mixtures thereof.

The cathodic casing 28 shown in Fig. 1 is cylindrical having a longitudinal axis and a circular base. The base, however can have any closed shape such as a square, rectangular or oval. Cathodic casing 28 is structured for positioning the cathode 20 in contact with the electrolyte 18 at a second contact surface area 24. Preferably the cathodic casing 28 has a similar base shape and base dimension to facilitate connection of the cathodic section 14 with the electrolyte 18 through gold gaskets 27. The material for the cathodic casing 28 is preferably alumina although other cylindrical inert temperature-resistant materials can be used.

Power output increases with an increase in the second contact surface area 24 which can be optimized when a substantially planar cathode 20 contacts a substantially planar electrolyte 18, as shown in Fig. 1. When both the electrolyte 18 and cathode 20 are layers, they can either have a flat or planar arrangement as shown in Fig. 2 or a tubular arrangement as shown in Fig. 3. The cathode has a thickness from the contact area with the electrolyte on one side of the cathode to a second side of the cathode exposed to oxygen, where the thickness is at least about 1 μm . The second contact surface area 24 increases substantially when electrolyte 18 is deposited onto the cathode 20 at the second contact surface area 24 by a method selected from the group consisting of screen-printing, painting, spraying, dipping, pressing, ion deposition, electrochemical vapor deposition, electron beam evaporation, green tape and sintering, plasma deposition, laser deposition and thermal deposition. This increase in second contact surface area 24 is achieved because of the intimate contact obtained at the interface between the cathode and electrolyte (the second contact surface area) using these methods.

The cathode 20 ionizes oxygen, O_2 , to oxygen anions, O^{2-} , at an oxygen ionization rate. The "oxygen ionization rate" is defined as a weight of oxygen ionized per unit time passing through a contact surface area (e.g., the second contact surface area 24 of Fig. 1). Preferably, the cathode 20 has an oxygen ionization rate of between about $10^{-8} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ and about $10^{-3} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$. More preferably, the oxygen ionization rate is between about $5 \times 10^{-6} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ and about $10^{-4} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$.

The cathode 20 is constructed of material that can withstand operating temperatures of

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at least about 400°C and has an electrical resistivity of between about 10⁹ ohm-cm and about 100 ohm-cm. Preferably, the cathode 20 may be selected from the group consisting of a metal, a metal oxide, a plurality of metal oxides and mixtures thereof. The metal is defined as a solid at a temperature of at least about 400°C and which retains inherent conductivity when exposed to oxygen at temperatures of at least about 400°C. The metal can be selected from the group consisting of platinum, palladium, gold, silver, steel, copper, nickel, cobalt, titanium, vanadium, chromium, iron, zirconium, rhodium, osmium and mixtures thereof.

5 Alternatively, the solid state cathode can be a ceramic material having a formula $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_b\text{C}_c\text{O}_d$ where A is an alkaline earth metal, B is selected from the group consisting of scandium, yttrium and a lanthanide metal (e.g., cerium, samarium, erbium, gadolinium), C is selected from the group consisting of titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, bismuth, hafnium, aluminum and antimony. An appropriate number of oxygen anions are required to counteract the positive charge on the metal ions to result in a neutrally-charged $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_b\text{C}_c\text{O}_d$ species. Because a metal is always present in the

10 formula, at least one of x, y, a, b and c is greater than zero where x is from 0 to about 1.05, y is from 0 to about 1, a is from 0 to about 0.5, b is from 0 to about 0.5, and c is from 0 to about 0.5. Oxide is always present in the formula, and d is between about 1 and about 5. Examples of solid state cathodes include LaMnO_3 , $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$, $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$, $\text{La}_{0.84}\text{Ba}_{0.16}\text{MnO}_3$, $\text{La}_{0.65}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$, $\text{La}_{0.79}\text{Sr}_{0.16}\text{Mn}_{0.85}\text{Co}_{0.15}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$,

15 $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$, $\text{La}_{0.6}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Al}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sc}_{0.16}\text{MnO}_3$, and $\text{La}_{0.84}\text{Y}_{0.16}\text{MnO}_3$. Cathode materials can also be a physical mixture of $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_b\text{C}_c\text{O}_d$ and another ceramic preferably having a formula $(\text{ZrO}_2)(\text{HfO}_2)_e(\text{Y}_2\text{O}_3)_f$ where e is from 0 to about 0.2 and f is from 0 to about 0.5. Preferably, the mixture has a ratio from 1:0 to about 1:2. For example a physical blend of $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$, with $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ can be prepared at a ratio from 1:0 to about 1:2. The physical blend is prepared by grinding the mixture with a mortar and pestle. The physical blend can also contain binding reagents such as water, polyols, polyesters, polysaccharides (starch), and polymers/solvents. All the metal oxide materials that make up the cathode are preferably subjected to a sintering step at temperatures of at least about

20 500°C. Upon sintering, the binder burns off.

25 The solid state cathode may also have a formula $\text{Li}_x\text{M}_{1-x}\text{O}$ where M is nickel or cobalt and x is from 0 to about 0.25. The solid state cathode can also be Cr_2O_3 .

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Referring to Figs. 4 and 5, the solid state cathode may be positioned against a substrate 42 which functions to enhance cathode strength and prevent peeling of the cathode. The substrate 42 is in contact with the cathode at a surface 44 opposite the second contact surface area 24, as shown in Figs. 4 and 5. The substrate is porous to oxygen, stable at operating temperatures of at least about 400 °C and can be selected from the group consisting of Al₂O₃, TiO₂, ZrO₂, zirconia stabilized by CaO, zirconia stabilized by Y₂O₃ and any of the cathode materials described previously.

Cathodic section 14 may also include an oxygen-containing gas flow pipe for directing an oxygen-containing gas flow toward the cathode 20. In Fig. 1, the oxygen-containing gas flow comprises a gas pipe 38 and a source of oxygen gas. Oxygen can also be supplied to the cathode simply by operating the unit in the air, which has an oxygen content of 23%. Air can also be directed towards the cathode at a flow rate of from 0 mL/min per Watt to about 2000 mL/min per Watt. The air pressure can range from about 0.01 atmospheres (atm) to about 1000 atm. Efficiency can be increased as the oxygen content increases. The oxygen-containing gas flow can have an oxygen content of between about 0.1% to about 100%. A metal wire lead 36 may be connected to the cathode 20.

The electrolyte 18 interfaces anode 16 and cathode 20. In Fig. 1, the electrolyte 18 is a solid state electrolyte which may be selected from the group consisting of a metal oxide and a plurality of metal oxides. The electrolyte is capable of oxygen ion conductivity. Preferably, at operational temperatures of about 400°C to about 2000°C, the electrolyte has an oxygen ion conductivity of at least about 0.001 S/cm, more preferably at least about 0.1 S/cm, even more preferably at least about 1.0 S/cm and more preferably still at least about 10 S/cm. Oxygen ion conductivity of solid state materials can be measured by standard methods known in the art.

The solid state electrolytes used are preferably ceramic materials. In one embodiment, the ceramic has a formula (ZrO₂)(HfO₂)_a(M'_uO_v)_c(Y₂O₃)_d(M''_xO_y)_e where a is from 0 to about 0.2, b is from 0 to about 1.0, c is from 0 to about 1.0, d is from 0 to about 0.5, e is from 0 to 0.15 and at least one of a, b, c, d or e is greater than zero. M (i.e. M' or M'') is selected from a group of divalent, trivalent or tetravalent metals consisting of manganese, iron, cobalt, nickel, copper, zinc, cerium, gadolinium, thorium, calcium, samarium, bismuth and tungsten. An appropriate number of oxygen anions are required to counteract the positive charge on the metal ions to give a neutrally-charged M_xO_y species. When c is greater than 0, u

and v can be the same or different and each is from about 0.2 to about 2.0. When e is greater than 0, x and y are integers greater than zero in which x is less than or equal to 2 and y is less than or equal to 3. One example of an electrolyte is ZrO₂, in which all of a, c, d and e equal zero and b = 1. Other examples of electrolytes include (ZrO₂)(Y₂O₃)_{0.08},

- 5 (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08}, (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.05}, (ZrO₂)(Y₂O₃)_{0.08}(Fe₂O₃)_{0.05},
(ZrO₂)(Y₂O₃)_{0.08}(CoO)_{0.05}, (ZrO₂)(Y₂O₃)_{0.08}(ZnO)_{0.05}, (ZrO₂)(Y₂O₃)_{0.08}(NiO)_{0.05}, (ZrO₂),
(CeO₂)_{0.8}(GdO_{1.5})_{0.2}, (ZrO₂)_{0.8}(CaO)_{0.13}, (ZrO₂)(Y₂O₃)_{0.08}(CuO)_{0.05}, and
(ZrO₂)(Y₂O₃)_{0.08}(MnO)_{0.05}. Electrolyte green tape may also be used, formed from a blend of
(ZrO₂)_b(HfO₂)_a(M'_uO_v)_c(Y₂O₃)_d(M''_xO_y)_e combined with a binder containing a maximum of
10 80% of at least one binder such as polymers/solvents, water, polyols, polyesters and
polysaccharides. All the metal oxide materials that make up the electrolyte are preferably
subjected to a sintering step at temperatures of at least 500 °C. Upon sintering, the binder
burns off.

The electrolyte may be a molten electrolyte, preferably having a melting temperature
15 of between about 300 °C and 2000 °C. The electrolyte may be selected from the group
consisting of metal carbonate, metal oxide, a plurality of metal carbonates, a plurality of metal
oxides and mixtures thereof. Examples of molten electrolytes include lithium carbonate,
sodium carbonate, potassium carbonate, strontium carbonate, barium carbonate, magnesium
carbonate, calcium carbonate, beryllium carbonate, cesium carbonate, rubidium carbonate,
20 PbCl₂·2PbO, PbO, Bi₂O₃, Bi₂O₅, molybdenum oxide, Cs₂O, Cs₂O₃, Sb₂O₃, Sb₂O₄, Sb₂O₅, CuO,
CuO₂, GeO₂, GeO, lithium oxide, palladium oxide, K₂O, KO₂, NaO₂, Na₂O₂, RbO₂, Rb₂O₃,
Rb₂O₂, SnO, SnO₂, tellurium oxide, Tl₂O, Tl₂O₃, vanadium oxide, As₄O₆, As₂O₅, In₂O, In₂O₃,
and mixtures thereof.

Fig. 6 shows a semidiagrammatic, cross-sectional view of an embodiment of an
25 electricity generating unit 50 having a molten electrolyte 56, a solid state cathode 52 and a
carbon-containing anode 54. The electrolyte 56 is contained within a ceramic housing 68.
Cathode 52 and anode 54 are partially immersed in electrolyte 56. Fig. 6 shows a solid anode
54. The anode 54 may also be in particulate form that would be positioned within a casing
before immersion into electrolyte 56. The casing is constructed such that molten electrolyte
30 can enter the casing to contact the particulate anode material while preventing the flow of
particulate material out into the molten electrolyte. Preferably an oxygen-containing gas flow
is bubbled into the electrolyte from inlet 66. Inlet 66 is situated to be in the closest possible

proximity to cathode 52 to minimize the distance that the oxygen must travel to reach cathode 52. Oxidant gases may exit the unit at outlets 58 and 60. Outlets 58 and 60 are preferably situated at an end of the ceramic housing 68 opposite inlet 66 to allow oxygen to flow throughout the length of the cathode 52 and maximize the use of the cathode surface. A 5 separator 59 allows most of the oxidant gases to exit through outlet 58 to prevent contacting anode 54, causing oxidation of anode 54. Exhaustive gases such as carbon dioxide and carbon monoxide can also exit through outlets 58 and 60. With separator 59, most of the exhaustive gases exit through outlet 60. Fig. 6 also shows a heater 62 surrounding the ceramic housing 68 to heat the unit 50 to operating temperatures of at least 400 °C. The heater may also 10 partially surround the ceramic housing 68 or heat a surface or a portion of a surface of the ceramic housing 68. The heater may be an external electric heater. The heater can also comprise burning the carbon monoxide exhaust gas or heating carbon anode 54 itself.

Fig. 7 shows another example of an electricity generating unit 10 having a solid carbon-containing anode 16, cathode 20 and solid-state electrolyte 18. Fig. 7 differs from Fig. 15 1 in that the cathode 20 and electrolyte 18 can be urged toward carbon-containing anode 16 by urging means, such as a spring 33 positioned under cap 31. Of course, any type of urging means can be contemplated. For example, a weight can be applied on casing 26 and a force, e.g., gravity, can be made to act upon the weight to urge electrolyte 18 into maximal contact 20 with carbon-containing anode 16. Or a clamp can be used to continuously urge the electrolyte 18 towards the carbon-containing anode 16. Other urging means can involve electromagnetic force, centrifugal force, hydraulic and pneumatic forces and other mechanical or electrical forces.

The arrangement shown in Fig. 7 has advantageous features, in particular where carbon-containing anode 16 comprises a particle form or a solid block or blocks of carbon. 25 During operation of the unit 10, solid carbon immediately surrounding electrolyte 18 is consumed over a period of time, resulting in a gap 41 between portions of anode 16 and electrolyte 18. Formation of gap 41 can reduce the first contact surface area 22 resulting in a decrease of the power output. By the arrangement of Fig. 7, the volume of gap 41 can be substantially reduced by urging electrolyte 18 towards carbon-containing anode 16, to 30 maximize the first contact surface area 22.

It has been discovered that the advantageous features provided by the arrangement of Fig. 7 results in an electricity generating unit that is constructed and arranged to be

continuously operable for at least about 10 hours (h), more preferably at least about 25 h, even more preferably at least about 50 h, and even more preferably still at least about 100 h. An electricity generating unit having the ability to be continuously operable for such extended periods of time can have a wide variety of applications as either a fuel cell or a battery.

Another aspect of the present invention provides a method for generating electricity in an electricity generating unit 10. The method comprises the steps of providing a carbon-containing anode 16, an electrolyte 18 in contact with the carbon-containing anode 16 at a first contact surface area 22 and a solid state cathode 20 in contact with the electrolyte 18 at a second contact surface area 24, as exemplified in Fig. 1. Oxygen is directed towards the cathode and the unit 10 is heated to temperatures between about 400 °C and about 2000 °C to cause electricity to be generated.

The method includes a step of directing an oxygen-containing gas flow towards the cathode.

The oxygen-containing gas flow provides oxygen to the cathode where oxygen is ionized to oxygen ions, according to the electrochemical half reaction shown in eq. 1:



Preferably, the cathode ionizes oxygen, O₂ to oxygen anions, O²⁻. Preferably, the cathode has an oxygen ionization rate of between about 10⁻⁸ g·s⁻¹·cm⁻² and about 10⁻³ g·s⁻¹·cm⁻². More preferably, the oxygen ionization rate is between about 5 x 10⁻⁶ g·s⁻¹·cm⁻² and about 10⁻⁴ g·s⁻¹·cm⁻². Oxygen anions can be released from the cathode to the electrolyte which interfaces the cathode. The electrolyte preferably allows the conduction of ions between the cathode and anode, such as the passage of oxygen anions to the anode. In Fig. 1 the electrolyte 18 is a solid state electrolyte. The solid state electrolyte can be selected from the group consisting of a metal oxide and a plurality of metal oxides. It is known that ions can move through a metal oxide by several mechanisms. For example, the metal ions and oxygen ions of a metal oxide can be roughly viewed as spheres that are packed in a regular array, leaving intrinsic channels and tunnels that provide passageways for ions. Moreover, metal oxides are not perfect solids in that they contain defects or holes. An ion can move from one site to a hole, leaving another hole in its wake that can be potentially occupied by another ion. Zirconia (ZrO₂), hafnia (HfO₂), yttrium-stabilized zirconia and yttrium-stabilized hafnia are

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commonly known as effective oxygen anion conducting materials. Moreover, substituting tetravalent zirconium ions, Zr^{4+} , in the crystal lattice with metal ions having valence numbers of less than four reduces a required number of oxygen anions in the lattice to achieve charge neutrality. Consequently, such doped materials have extra oxygen anion vacancies in the
5 crystal lattice.

Efficiency increases when ions travel a smaller distance through the solid state electrolyte. Cell efficiency is optimized as a dimension between the first contact surface area and the second contact area is minimized. The electrolyte is a substantially planar material and a dimension from the first contact area to the second contact area is between about 1 μm
10 to about 1000 μm , preferably between about 1 μm and about 600 μm and more preferably between about 1 μm and about 100 μm .

Ionic mobility in a solid is relatively low compared to ionic mobility in a molten state medium. Preferably, the electrolyte is a molten state electrolyte in which the electrolyte has a melting point of between about 300 °C and 2000 °C.

15 The method also comprises using carbon as a fuel source, wherein the carbon fuel source also acts as an anode and undergoes a first electrochemical half reaction as shown in eq. 2 when allowed to react with a sufficient amount of oxygen anions:



20 Alternatively, carbon can undergo a second electrochemical half reaction as shown in eq. 3:



25 The reaction of eq. 3 occurs when a small amount of oxygen anions is present, the small amount being less than the sufficient amount of oxygen required in eq. 2. The anode can be in solid form or in particulate form. When the anode is in particulate form, a device may be provided to urge the anode against the electrolyte to increase the second contact surface area.
30 The device may be a spring or any urging device that uses any one or a combination of gravitational force, electromagnetic force, electrical force, centrifugal force, hydraulic and pneumatic forces and any other mechanical forces. Examples of electrical devices include

motors such as stepping motors. Examples of electromagnetic devices include relays and magnets. It is known that power output increases as the second contact surface area increases.

The method includes the step of heating the electricity generating unit to temperatures between about 400 °C and about 2000 °C, preferably between about 700 °C and about

5 1200°C. There exists a high activation energy barrier in a reaction between carbon or any carbon cation with oxygen anions to yield products such as carbon monoxide or carbon dioxide. The energy to overcome the activation energy barrier may be supplied as heat energy. Fig. 1 shows a heater 40 surrounding the anodic casing 26 and cathodic casing 28. The heater 40 may also surround a portion of both the anodic casing 26 and cathodic casing
10 28 that includes anode 16, electrolyte 18 and cathode 20, or the heater 40 may contact a portion of a surface of anodic casing 26 and cathodic casing 28 that includes anode 16, electrolyte 18 and cathode 20. The heater may be an external electric heater. The heater can also comprise burning the carbon monoxide exhaust gas, any fuel or heating the carbon anode 20 itself. The heater is capable of heating the unit to a temperature of between about 400 °C
15 and about 2000 °C. Preferably the heater heats the unit at a temperature of between about 700 °C and about 1200 °C.

In one embodiment, the interface between the electrode and the anode has a layer of a metal that can function as a catalyst to catalyze a reaction between carbon or any carbon cation with oxygen anions. Referring back to Fig. 1, the metal layer can be positioned on the
20 first contact surface area 22. Preferably, the metal is unreactive towards the carbon anode itself. Examples of such metals include platinum, rhodium and palladium. By this embodiment, it is believed that the addition of a metal catalyst can increase an electrical output of the unit as well as increasing the reaction rate between a carbon-based species and oxygen anions. Preferably, the metal layer has a thickness of less than about 5000 µm, more
25 preferably less than about 1000 µm and more preferably less than about 10 µm.

In Fig. 1, metal wire leads 34 and 36 are provided. Metal wire lead 36 is directly connected to the cathode 20 and metal wire lead 34 is connected to the spring 32 which has a surface 35 to contact the anode 16. Where the spring 32 also functions as a current collector, preferably, the spring 32 has a resistivity which is at least equal to that of the anode 16. When
30 the anode is a solid, the spring 32 may be connected directly to the anode. The metal wire leads 34 and 36 may be selected from the group consisting of platinum, copper, silver, steel, conductive ceramics and metal oxides, and graphite. When one end of each metal wire lead is

connected to the anode or cathode, the other end may be connected to a load. At a temperature of at least 400 °C, the unit 10 provides an electrical output of at least 1 mW·cm⁻² of the second contact surface area, preferably of from about 1 mW·cm⁻² to about 5000 mW·cm⁻² of the second contact surface area, more preferably of from about 10 mW·cm⁻² to about 5000 mW·cm⁻² of the second contact surface area and more preferably still of from about 100 mW·cm⁻² to about 5000 mW·cm⁻² of the second contact surface area.

The function and advantage of these and other embodiments of the present invention will be more fully understood from the examples below. The following examples are intended to illustrate the benefits of the present invention, but do not exemplify the full scope 10 of the invention.

Example 1: A La_{0.84}Sr_{0.16}MnO₃ Cathode:

A cathode material as shown in Fig. 1 was prepared with a spray dryer. All chemical reagents were purchased from Alfa Aesar, Ward Hill, MA. Lanthanum nitrate (hexahydrate, 15 26.0 g) strontium nitrate (3.4 g) and manganese acetate (tetrahydrate, 24.5 g) were dissolved in 150 mL of water to give a molar ratio of 0.84:0.16:1 for La:Sr:Mn. The solution was sprayed into a hot chamber to vaporize the volatile components. The residual was then sintered at 1000 °C for one hour to achieve fine uniform particles having a particle size of 0.01 - 2 microns. The cathode material was combined with a binder, starch, and pressed into a disk 20 having a diameter of 12.5 mm.

Example 2: A La_{0.84}Sr_{0.16}MnO₃ Cathode/(ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08} Electrolyte Cell:

A 12.5 mm diameter and 600 μm thick planar cathode disk of La_{0.84}Sr_{0.16}MnO₃ as prepared in Example 1 was painted, with a thin layer of slurry containing (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08} (1.0 g), glycerin (0.5 g) and starch (0.2 g) in 5 mL water and 25 sintered at 1100 °C to form a dense electrolyte having a thickness of 100 μm.

Example 3: Cathode Materials from La_{0.84}Sr_{0.16}MnO₃/(ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08} blends

La_{0.84}Sr_{0.16}MnO₃ (1.0 g) is combined with (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08} (0.1 g) and ground 30 with a mortar and pestle. An amount of 0.18 g of the ground material was used to make a 12.5 mm and 600 μm disk by pressing. The disk was sprayed with (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08} powder (0.05 g), pressed again and sintered at 1100 °C for 1 h to form a 120 μm thick planar

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electrolyte. Similar blends can be prepared by combining $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ (1.0 g) with $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ (0.2 g), $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ (1.0 g) with $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ (0.5 g), and $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ (1.0 g) with $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ (1.0 g).

5 Example 4: A $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ Cathode/ $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ Electrolyte Cell with Substrate:

CaO stabilized zirconia (1.0 g, 4 wt%), purchased from Alfa Aesar, Ward Hill, MA, was combined with polysaccharide (0.2 g) and ground with a mortar and pestle to form a blend. The blend (0.3 g) was molded and pressed into a 12.5 mm disc. The substrate disc was sprayed with a thin layer of the cathode material from Example 1 (0.05g), pressed again, fired and sintered at 1000 °C for one hour. The disc was cooled down and painted with the electrolyte material of Example 2 to give a film thickness of 125 µm and fired and sintered at 1100 °C for 1 h.

15 Example 5: A Solid State Electrolyte Fuel Cell - 1

A 12 mm diameter fuel cell disk from Example 3 consisting of a 200 µm thick 1:1 $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3/(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ cathode blend and a 600 µm thick $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ electrolyte was used as a cathode/electrolyte cell in the structure of Fig. 1. Carbon black, obtained as Black Pearl from Cabot Corp., Boston, MA was used as the anode in an amount of 1.0 g. Platinum wires were connected to the anode and cathode and attached to a multimeter. Nitrogen gas was used to blanket the carbon anode at a flow rate of 2 mL/min. Air was supplied to the cathode at a rate of 10 mL/min. The solid state cathode, electrolyte and anode combination was mounted in a structure as shown in Fig. 1 where the casings 26 and 28 have an inner diameter of 8 mm. The fuel cell was heated to 1000°C to generate an electric current of 10 mW·cm⁻² power output with a voltage of 0.362 V.

25 Example 6: A Solid State Electrolyte Fuel Cell - 2

A 12 mm diameter fuel cell disk from Example 3 consisting of a 200 µm thick 1:0.25 $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3/(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ cathode blend and a 600 µm thick $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ electrolyte was used as a cathode/electrolyte cell in the structure of Fig. 1 where the casings 26 and 28 have an inner diameter of 8 mm. Graphite (1.0 g) obtained as TIMREX KS 5-75TT from Timcal America Inc., Ohio, was used as the anode. Platinum

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wires were connected to the anode and cathode and attached to a multimeter. Nitrogen gas was used to blanket the carbon anode at a flow rate of 2 mL/min. Oxygen was supplied to the cathode by direct exposure to air. The fuel cell was heated to 800°C to generate an electric current of 2.5 mW·cm⁻² power output with a voltage of 0.362 V. At 1019 °C, the fuel cell generated an electric current of 12 mW·cm⁻² power output with a voltage of 0.44 V.

5

Example 7: A Solid State Electrolyte Fuel Cell - 3

An 11.5 mm fuel cell disk from Example 3 consisting of a 600 µm thick La_{0.84}Sr_{0.16}MnO₃ cathode and a 120 µm thick (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08} electrolyte was used as a cathode/electrolyte cell in the structure of Fig. 1 where the casings 26 and 28 have an inner diameter of 8 mm. Carbon black, obtained as Black Pearl from Cabot Corp., Boston, MA was used as the anode in an amount of 1.0 g. Platinum wires were connected to the anode and cathode and attached to a multimeter. No inert gas was supplied to the anode. Oxygen was supplied to the cathode by direct exposure to air. The fuel cell was heated to 800°C to generate an electric current of 10 mW·cm⁻² power output with a voltage of 0.248 V. At 1002 °C, the fuel cell generated an electric current of 50 mW·cm⁻² power output with a voltage of 0.507 V.

10

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Example 8: A Molten State Electrolyte Fuel Cell - 1

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Referring to Fig. 6, a fuel cell having a Pt foil cathode activated with Pt black and an electrically conductive carbon rod anode was prepared. The anode was prepared by combining carbon powder with a polysaccharide (starch) binder. Carbon black (80 wt %), obtained as Black Pearl from Cabot Corp., Boston, MA and starch (20 wt %) were combined and ground with a mortar and pestle and pressed into a rod of 1 cm diameter having a length of 10 cm. The carbon rod was heated to 1000 °C at a rate of 100 °C/h under a nitrogen atmosphere. The electrolyte was lithium carbonate purchased from Aldrich, WI. The components were stored in a ceramic cell housing. The cell housing was placed in a controlled heating block and heated up to 900 °C. A 70:30 v:v oxygen/carbon dioxide gas flow was bubbled at a rate of 10 mL/min through an inlet under the cathode.

Example 9: A Molten State Electrolyte Fuel Cell - 2

A fuel cell having an arrangement as described in Example 8 using a NiO cathode was prepared by combining NiO powder with lithium oxide in a 1:0.05 ratio, both NiO and lithium oxide purchased from Aldrich, Milwaukee, WI. A starch binder (20 wt %) was added and the mixture was pressed into a rod having a length of 10 cm and a diameter of 1 cm. The tube
5 was placed in a furnace and heated to 1100°C at rate of 100°C/h in air. The anode was prepared by heating smokeless coal to 1000°C under an inert atmosphere to form coke. The coke was crashed and ground into a powder. Coke (80 wt %) and starch (20 wt %) were ground with a mortar and pestle and pressed into a 10 cm long rod having a diameter of 1 cm.
10 The carbon anode was heated to 1000°C. The electrolyte was lithium carbonate containing 5 wt % strontium carbonate stored in a ceramic cell housing up to 900°C. A 80:20 v:v air/carbon dioxide gas flow was bubbled at a rate of 10 mL/min through an inlet under the cathode.

15 Example 10: a Molten State Electrolyte Fuel Cell - 3

A fuel cell having an arrangement as described in Example 8 using a Bi_2O_3 electrolyte purchased from Aldrich, Milwaukee, WI was prepared. The fuel cell had a platinum foil cathode activated with platinum black and an electrically conductive carbon rod anode. Carbon black (80 wt %) obtained as Black Pearl from Cabot Corp., Boston, MA and starch (20 wt %) were ground with a mortar and pestle, molded and pressed into a 10 cm long rod having a diameter of 1 cm. The carbon rod was heated to 1000°C at a rate of 100°C/h under a nitrogen atmosphere. The components were stored in a ceramic cell housing. The cell housing was placed in a controlled heating block and heated up to 1100°C. An air flow was bubbled at a rate of 10 mL/min through an inlet under the cathode.

25

Example 11

A 12 mm diameter electrochemical cell disk from Example 1 consisting of a 30 mm thick $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ cathode and a 500 mm thick $(\text{ZrO}_2)_{1.0}(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ electrolyte was used as a cathode/electrolyte cell in the structure of Fig. 7. Carbon Black, obtained as Black Pear from Cabot Corp., Boston, MA, was used as the anode in an amount of 10 grams. Platinum wire was connected to the cathode and graphite rod was connected to the anode and attached to a load. Exhaustive gases produced during run were used to blanket the carbon

anode. Air was supplied to the cathode at a rate 20 mL/min. The solid state cathode, electrolyte and anode combination was mounted in a structure as shown in Fig. 7 where the casing 26 has an inner diameter of 8 mm. The cell was heated to temperatures of 900°C, 1000°C and 1100°C to generate an electric current with voltages of 0.87 V, 0.97 V and 1.05 V
5 respectively.

Example 12

A 12 mm diameter electrochemical cell disk from Example 1 consisting of a 30 mm thick $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ cathode and a 500 nm thick $(\text{ZrO}_2)_{1.0}(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ electrolyte was
10 used as a cathode/electrolyte cell in the structure of Fig. 7. On the surface of the electrolyte, a thin layer of platinum black 10 nm was coated between the electrolyte and the anode carbon. Carbon Black, obtained as Black Pear from Cabot Corp., Boston, MA, was used as the anode in an amount of 5 grams. Platinum wire was connected to the cathode and graphite rod was connected to the anode and attached to a load. Exhaustive gases produced during run were
15 used to blanket the carbon anode. Air was supplied to the cathode at a rate 20 mL/min. The solid state cathode, electrolyte and anode combination was mounted in a structure as shown in Fig. 7 where the casing 26 has an inner diameter of 8 mm. The cell was heated to 1100°C to generate an electric current of 180 mw/cm² power output with a voltage of 1.06 volts. The cell ran continuously for 120 hours between temperatures of 850°C and 1100°C.

20

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that actual parameters will depend upon the specific application for which the methods and apparatus of the present invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that,
25 within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described. For example, the anode, cathode and solid electrolyte can be in various regular or irregular geometric shapes such as cylinders, rectangles, five, six, seven, eight or more-sided shapes, planar or curved layers and others.

30 What is claimed is:

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CLAIMS

1. An electricity-generating unit comprising:
a carbon-containing anode;
an electrolyte in contact with said anode at a first contact surface area, allowing
passage of oxygen anions to said anode; and
a solid state cathode in contact with said electrolyte at a second contact surface area,
for ionizing oxygen to oxygen anions, said unit being operable at a temperature of between
about 400 °C and about 2000 °C.

10 2. An electricity-generating unit, comprising:
a carbon-containing anode;
an electrolyte in contact with said anode at a first contact surface area;
a solid state cathode in contact with said electrolyte at a second contact surface area;
15 a heater constructed and arranged to heat said anode to a temperature of between about
400°C and about 2000°C; and
a source of an oxygen-containing gas positioned to provide said gas to said cathode to
produce an electrical output of at least about $1 \text{ mW}\cdot\text{cm}^{-2}$ of said second contact surface area.

20 3. An electricity-generating unit comprising:
a carbon-containing anode;
an electrolyte in contact with said anode at a first contact surface area, allowing
passage of oxygen anions to said anode; and
a solid state cathode in contact with said electrolyte at a second contact surface area,
25 for ionizing oxygen to the oxygen anions, said unit being constructed and arranged to be
continuously operable for at least about 10 hours.

4. The unit as in either of claim 1 or claim 2, wherein said unit is continuously operable
for at least about 10 hours.

30 5. The unit as in claim 3, wherein said unit is operable at a temperature of between about
400°C and about 2000°C.

6. The unit as in any preceding claim, wherein said unit is operable at a temperature of between about 700 °C and about 1200 °C.
7. The unit as in any preceding claim, wherein said unit is continuously operable for at least about 25 hours.
- 5
8. The unit as in any preceding claim, wherein said unit is continuously operable for at least about 50 hours.
- 10 9. The unit as in any preceding claim, wherein said unit is continuously operable for at least about 100 hours.
- 15 10. The unit as in any of claims 1 and 3-9, wherein said unit has an electrical output of at least about 1 mW·cm⁻² of said second contact surface area.
11. The unit as in any preceding claim, wherein said unit has an electrical output of from about 1 mW·cm⁻² to about 5000 mW·cm⁻² of said second contact surface area.
- 20 12. The unit as in any preceding claim, wherein said unit has an electrical output of from about 10 mW·cm⁻² to about 5000 mW·cm⁻² of said second contact surface area.
13. The unit as in any preceding claim, wherein said anode comprises conductive carbon having a resistivity of between about 10⁻⁵ ohm-cm to about 100 ohm-cm.
- 25 14. The unit as in any preceding claim, wherein said anode comprises conductive carbon having a resistivity of between about 10⁻³ ohm-cm to about 10⁻¹ ohm-cm.
15. The unit as in any preceding claim, wherein said anode is a solid material.
- 30 16. The unit as in any preceding claim, wherein said anode is selected from the group consisting of graphite, quasi-graphite, coal, coke, charcoal, fullerene, buckminsterfullerene, carbon black, activated carbon, decolorizing carbon, other carbons derived from wood and

natural biomass and mixtures thereof.

17. The unit as in any preceding claim, wherein said electrolyte is a solid state electrolyte.

5 18. The unit as in any preceding claim, wherein said electrolyte has an oxygen ion conductivity of at least about 0.001 S/cm.

19. The unit as in any preceding claim, wherein said electrolyte has an oxygen ion conductivity of at least about 0.1 S/cm.

10 20. The unit as in any preceding claim, wherein said electrolyte has an oxygen ion conductivity of at least about 1.0 S/cm

15 21. The unit as in any preceding claim, wherein said electrolyte has an oxygen ion conductivity of at least about 10 S/cm.

22. The unit as in any preceding claim, wherein said electrolyte defines a dimension therethrough from said first contact surface area to said second contact surface area of between about 1 μm and about 1000 μm .

20 23. The unit as in any preceding claim, wherein said electrolyte defines a dimension therethrough from said first contact surface area to said second contact surface area of between about 1 μm and about 600 μm .

25 24. The unit as in any preceding claim, wherein said electrolyte defines a dimension therethrough from said first contact surface area to said second contact surface area of between about 1 μm and about 100 μm .

25 25. The unit as in any preceding claim, wherein said solid state electrolyte is selected from 30 the group consisting of a metal oxide and a plurality of metal oxides.

26. The unit as in any preceding claim, wherein said solid state electrolyte has a formula

(ZrO₂)(HfO₂)_a(M'_uO_v)_c(Y₂O₃)_d(M''_xO_y)_e where a is from 0 to about 0.2, b is from 0 to about 1.0, c is from 0 to about 1.0, d is from 0 to about 0.5, e is from 0 to about 0.15, and at least one of a, b, c, d and e is greater than zero, u is from about 0.2 to about 2.0, v is from about 0.2 to about 2.0, x is an integer greater than 0 and less than or equal to 2, y is an integer greater than 0 and less than or equal to 3, and M' and M'' can be the same or different and each is selected from the group consisting of manganese, iron, cobalt, nickel, copper, zinc, calcium, cerium, thorium, bismuth, gadolinium, samarium and tungsten.

27. The unit as in any preceding claim, wherein said solid state electrolyte is selected from the group consisting of (ZrO₂), (ZrO₂)(Y₂O₃)_{0.08}, (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.08}, (ZrO₂)(HfO₂)_{0.02}(Y₂O₃)_{0.05}, (ZrO₂)(Y₂O₃)_{0.08}(Fe₂O₃)_{0.05}, (ZrO₂)(Y₂O₃)_{0.08}(CoO)_{0.05}, (ZrO₂)(Y₂O₃)_{0.08}(ZnO)_{0.05}, (ZrO₂), (CeO₂)_{0.8}(GdO_{1.5})_{0.2}, (ZrO₂)_{0.87}(CaO)_{0.13}, (ZrO₂)(Y₂O₃)_{0.08}(NiO)_{0.05}, (ZrO₂)(Y₂O₃)_{0.08}(CuO)_{0.05}, and (ZrO₂)(Y₂O₃)_{0.08}(MnO)_{0.05}.

15 28. The unit as in any preceding claim, wherein said electrolyte is a blend comprising (ZrO₂)(HfO₂)_a(M'_uO_v)_c(Y₂O₃)_d(M''_xO_y)_e and a maximum of 80% of at least one binder selected from the group consisting of water, polyols, polyesters, polysaccharides, polymers and solvents prior to sintering.

20 29. The unit as in any preceding claim, wherein said electrolyte has a melting temperature of between about 300 °C and about 2000 °C.

30. The unit as in any preceding claim, wherein said electrolyte is selected from the group consisting of metal carbonate, metal oxide, a plurality of metal carbonates, a plurality of metal oxides and mixtures thereof.

31. The unit as in any preceding claim, wherein said electrolyte is selected from the group consisting of lithium carbonate, sodium carbonate, potassium carbonate, strontium carbonate, barium carbonate, magnesium carbonate, calcium carbonate, beryllium carbonate, cesium carbonate, rubidium carbonate, PbCl₂·2PbO, PbO, Bi₂O₃, Bi₂O₅, molybdenum oxide, Cs₂O, Cs₂O₃, Sb₂O₃, Sb₂O₄, Sb₂O₅, CuO, CuO₂, GeO₂, GeO, lithium oxide, palladium oxide, K₂O, KO₂, NaO₂, Na₂O₂, RbO₂, Rb₂O₃, Rb₂O₂, SnO, SnO₂, tellurium oxide, Tl₂O, Tl₂O₃, vanadium

oxide, As_4O_6 , As_2O_5 , In_2O , In_2O_3 , and mixtures thereof.

32. The unit as in any preceding claim, wherein said solid state cathode has an oxygen ionization rate of between about $10^{-8} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ and about $10^{-3} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$.

5

33. The unit as in any preceding claim, wherein said solid state cathode has an oxygen ionization rate of between about $5 \times 10^{-6} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ and about $10^{-4} \text{ g}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$.

34. The unit as in any preceding claim, wherein said solid state cathode has an electrical resistivity of between about $10^9 \text{ ohm}\cdot\text{cm}$ and about $100 \text{ ohm}\cdot\text{cm}$.
10

35. The unit as in any preceding claim, wherein said solid state cathode is selected from the group consisting of a metal, a metal oxide, a plurality of metal oxides and mixtures thereof.
15

36. The unit as in any preceding claim, wherein said solid state cathode is selected from the group consisting of platinum, palladium, gold, silver, steel, copper, nickel, cobalt, titanium, vanadium, chromium, iron, zirconium, rhodium and osmium.

20 37. The unit as in any preceding claim, wherein said solid state cathode has a formula $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_b\text{C}_c\text{O}_d$ where A is an alkaline earth metal, B is selected from the group consisting of scandium, yttrium and a lanthanide metal, C is selected from the group consisting of titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, bismuth, hafnium, aluminum and antimony, x is from 0 to about 1.05, y is from 0 to about 1, a is from 0 to about 0.5, b is from 0 to about 0.5, c is from 0 to about 0.5 and d is between about 1 and 25 about 5, and at least one of x, y, a, b and c is greater than zero.

38. The unit as in any preceding claim, wherein said solid state cathode is selected from the group consisting of LaMnO_3 , $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$, $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$, $\text{La}_{0.84}\text{Ba}_{0.16}\text{MnO}_3$,
30 $\text{La}_{0.65}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$, $\text{La}_{0.79}\text{Sr}_{0.16}\text{Mn}_{0.85}\text{Co}_{0.15}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$,
 $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$,
 $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$, $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$, $\text{La}_{0.6}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Al}_{0.2}\text{O}_3$,

$\text{La}_{0.84}\text{Sc}_{0.16}\text{MnO}_3$, and $\text{La}_{0.84}\text{Y}_{0.16}\text{MnO}_3$.

39. The unit as in any preceding claim, wherein said solid state cathode is a physical mixture of $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_w\text{C}_t\text{O}_d$ and $(\text{ZrO}_2)(\text{HfO}_2)_e(\text{Y}_2\text{O}_3)_f$ at a ratio from 1 : 0 to about 1 : 2 where e is from 0 to about 0.2 and f is from 0 to about 0.5.

40. The unit as in any preceding claim, wherein said physical mixture further comprises a binding reagent selected from the group consisting of water, polyols, polyesters, polysaccharides, polymer and solvents prior to sintering.

41. The unit as in any preceding claim, wherein said solid state cathode has a formula $\text{Li}_x\text{M}_{1-x}\text{O}$ where M is a metal selected from the group consisting of nickel and cobalt and x is from 0 to about 0.25.

42. The unit as in any preceding claim, wherein said solid state cathode is Cr_2O_3 .

43. The unit as in any preceding claim, wherein said solid state cathode has a thickness of at least about 1 μm .

44. The unit as in any preceding claim, further comprising a substrate in contact with said solid state cathode at a surface other than said second contact surface area, for providing support to said cathode.

45. The unit as in claim 44, wherein said substrate is selected from the group consisting of Al_2O_3 ; TiO_2 ; ZrO_2 ; zirconia stabilized by CaO ; zirconia stabilized by Y_2O_3 ; platinum; palladium; gold; silver; steel; copper; nickel; cobalt; titanium; vanadium; chromium; iron; zirconium; rhodium; osmium; $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_w\text{C}_t\text{O}_d$ where A is an alkaline earth metal, B is selected from the group consisting of scandium, yttrium and a lanthanide metal, C is selected from the group consisting of titanium, vanadium, chromium, iron, cobalt, nickel, copper, zinc, zirconium, bismuth, hafnium, aluminum and antimony, x is from 0 to about 1.05, y is from 0 to about 1, a is from 0 to about 0.5, b is from 0 to about 0.5, c is from 0 to about 0.5 and d is between about 1 and about 5, and at least one of x, y, a, b and c is greater than zero; LaMnO_3 ;

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$\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$; $\text{La}_{0.84}\text{Ca}_{0.16}\text{MnO}_3$; $\text{La}_{0.84}\text{Ba}_{0.16}\text{MnO}_3$; $\text{La}_{0.65}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Co}_{0.2}\text{O}_3$;
 $\text{La}_{0.79}\text{Sr}_{0.16}\text{Mn}_{0.85}\text{Co}_{0.15}\text{O}_3$; $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$; $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$;
 $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Ce}_{0.2}\text{O}_3$; $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$; $\text{La}_{0.84}\text{Sr}_{0.16}\text{Mn}_{0.8}\text{Cr}_{0.2}\text{O}_3$;
5 $\text{La}_{0.6}\text{Sr}_{0.35}\text{Mn}_{0.8}\text{Al}_{0.2}\text{O}_3$; $\text{La}_{0.84}\text{Sc}_{0.16}\text{MnO}_3$; $\text{La}_{0.84}\text{Y}_{0.16}\text{MnO}_3$; and a physical mixture of
 $\text{La}_x\text{Mn}_y\text{A}_z\text{B}_w\text{C}_v\text{O}_d$ and $(\text{ZrO}_2)(\text{HfO}_2)_e(\text{Y}_2\text{O}_3)_f$ at a ratio from 1 : 0 to about 1 : 2 where e is from
0 to about 0.2 and f is from 0 to about 0.5.

46. The unit as in any preceding claim, further comprising a source of an inert gas to isolate said anode from a surrounding environment.

10

47. The unit as in any preceding claim, further comprising a source for directing an oxygen-containing gas flow to said solid state cathode.

15

48. The unit as in any preceding claim, further comprising an urging device in operative relationship to said anode and acting to increase said first contact surface area.

20

49. The unit as in claim 48, wherein the said urging device is selected from the group consisting of a mechanical device, an electromagnetic device, an electrical device, a centrifugal device, a gravitational device and a hydraulic and pneumatic device.

25

50. The unit as in either claim 48 or 49, wherein said urging device is selected from the group consisting of a clamp, a spring, a stepping motor, a relay and a magnet.

51. The unit as in any preceding claim, further comprising a heater positioned to heat at least a portion of said unit to a temperature of between about 400°C and about 2000°C.

30

52. The unit as in any preceding claim, wherein said unit is capable of a voltage of at least about 0.1 volts.

53. The unit as in any preceding claim, wherein said unit is capable of a voltage of at least about 0.5 volts.

54. The unit as in any preceding claim, wherein said unit is capable of a voltage of at least about 1.0 volts.

5 55. The unit as in any preceding claim, further comprising a metal layer positioned on said first contact surface area for catalyzing a reaction between carbon ions and oxygen ions, the metal being unreactive with said carbon-containing anode.

10 56. The unit as in claim 55, wherein the metal layer is selected from the group consisting of platinum, rhodium and palladium.

57. The unit as in either claim 55 or claim 56, wherein the metal layer has a thickness of less than about 5000 μm .

15 58. The unit as in claim 57, wherein the metal layer has a thickness of less than about 10 μm .

20 59. A method for generating electricity in a unit, said method comprising:
providing a carbon-containing anode;
providing an electrolyte in contact with said carbon-containing anode at a first contact surface area;
providing a solid state cathode in contact with said electrolyte at a second contact surface area;
exposing said cathode to an oxygen-containing gas flow; and
heating said unit to a temperature of between about 400 °C and about 2000 °C to
25 produce an electrical output of at least about 1 $\text{mW}\cdot\text{cm}^2$ of said second contact surface area.

60. A method as in claim 59, wherein said electrolyte is provided as a solid state electrolyte.

30 61. A method as in either claim 59 or claim 60, wherein said solid state electrolyte is deposited onto said cathode at said second contact surface area by a method selected from the group consisting of screen-printing, painting, spraying, dipping, pressing, ion deposition,

electron beam evaporation, green tape and sintering, plasma deposition, electrochemical vapor deposition, laser deposition and thermal deposition.

62. A method as in any of claims 59-61, said anode being in solid form, the method
5 further comprising urging said anode solid into contact with said electrolyte to increase said
first contact surface area.

63. A method as in any of claims 59-62, said anode being in particle form, the method
further comprising urging said anode particles into contact with said electrolyte to increase
10 said first contact surface area.

64. A method as in either claim 62 or claim 63, wherein said urging is aided by gravity.

65. A method as in either claim 62 or claim 63, wherein said urging is executed by a
15 clamp.

66. A method as in either claim 62 or claim 63, wherein said urging is executed by a
spring.

20 67. A method as in either claim 62 or claim 63, wherein said urging is executed by a
device selected from the group consisting of a mechanical device, an electromagnetic device,
an electrical device, a centrifugal device, and a hydraulic and pneumatic device.

25 68. A method as in claim 67, wherein said device is selected from the group consisting of
stepping motors, relays and magnets.

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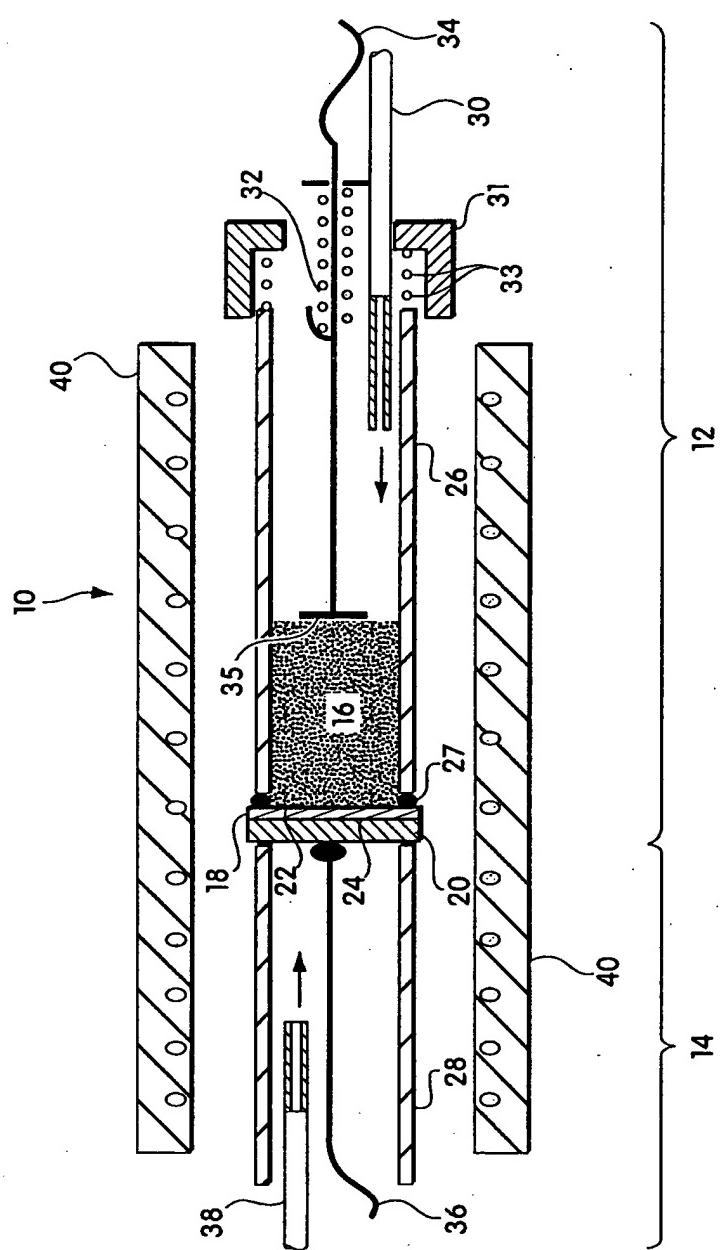


Fig. 1

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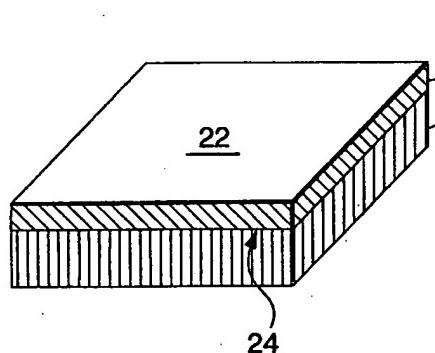


Fig. 2

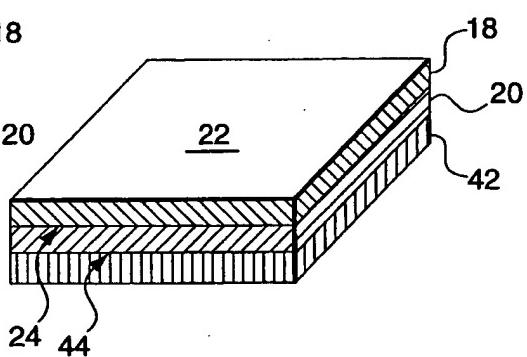


Fig. 4

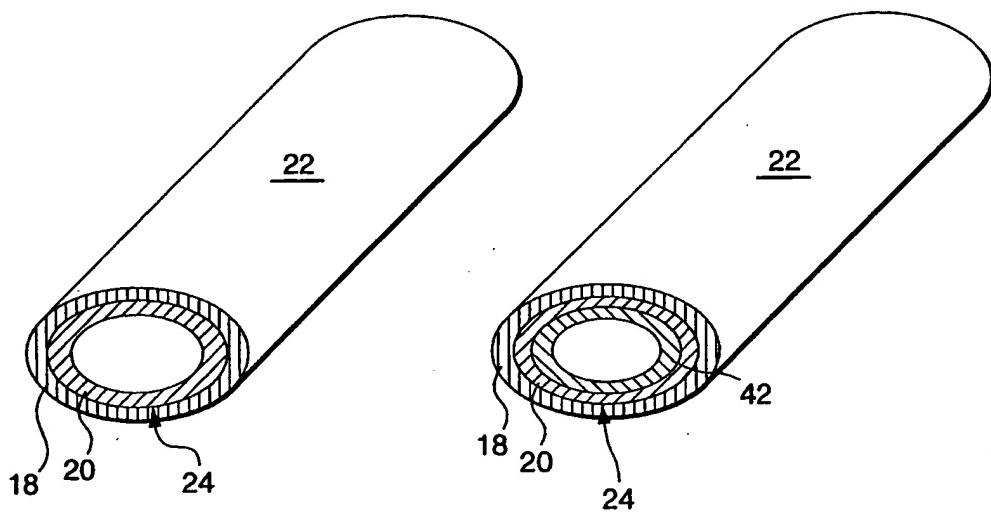


Fig. 3

Fig. 5

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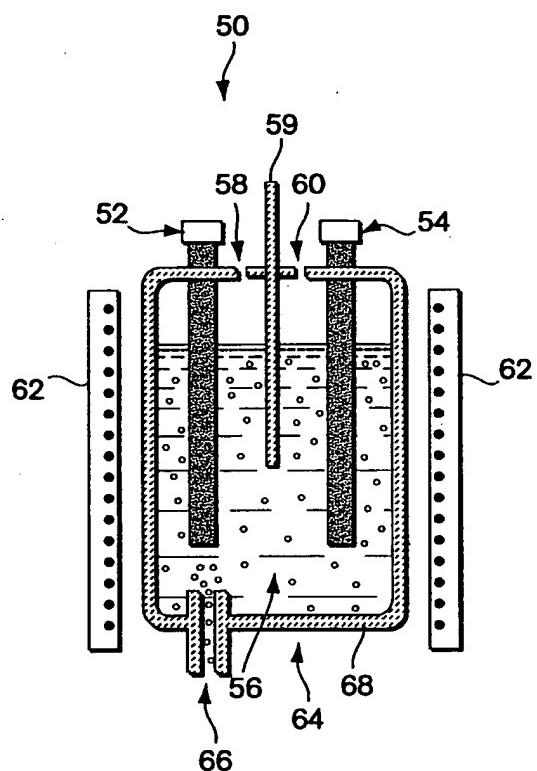


Fig. 6

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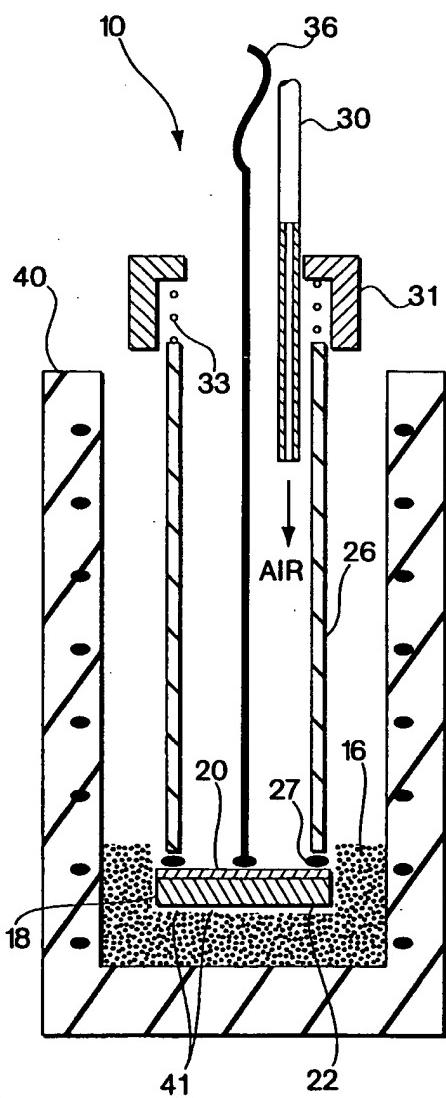


Fig. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/04741

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01M8/12 H01M8/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 95 09450 A (UNIV LELAND STANFORD JUNIOR) 6 April 1995 (1995-04-06) the whole document ----- -/-	1-6, 10, 13-19, 22, 25-27, 32-38, 43, 46, 47, 51-57, 59, 60, 62, 63

 Further documents are listed in continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search

20 July 1999

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 4 170 534 A (FITTERER GEORGE R) 9 October 1979 (1979-10-09) claims 1-4, 7-9, 11; figure 2 column 5, line 4 - column 6, line 19	1-6, 10, 14-18, 25-27, 32, 43, 47-54, 59, 62, 66, 67
X	GB 2 278 010 A (AGENCY IND SCIENCE TECHN) 16 November 1994 (1994-11-16) page 1, line 5 - line 14; claims 1, 2, 6; figures 1, 4 page 8, line 3 - line 18 page 8, line 21 - page 9, line 22 page 10, line 23 - page 11, line 15 page 13, line 7 - line 17; example 1 page 17, line 18 - line 23; figure 5	1-3, 5, 6, 10, 13-18, 25-27, 32, 35, 36, 46-52, 59, 60, 62, 65, 67
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International Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 3 138 490 A (WILLIAM E TRAGERT ET AL) 23 June 1964 (1964-06-23) claim 2; table I column 2, line 25 - line 50; figure 1 column 3, line 14 - line 31 column 3, line 50 - line 74 ---	1-9,17, 18, 25-27, 47, 51-56, 59,60
X	YENTEKAKIS I V ET AL: "A NOVEL FUSED METAL ANODE SOLID ELECTROLYTE FUEL CELL FOR DIRECT COAL GASIFICATION: A STEADY-STATE MODEL" INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH, vol. 28, no. 9, 1 September 1989 (1989-09-01), pages 1414-1424, XP000114234 ISSN: 0888-5885 abstract page 1415, left-hand column, paragraph 3 - right-hand column, paragraph 4; figure 1 page 1419, left-hand column, paragraph 2 ---	1-3,5,6, 17, 25-27, 34-38, 47,52, 59,60
X	EP 0 333 261 A (COSTA BRUNO) 20 September 1989 (1989-09-20) column 9, line 9 - line 26; claims 1-3 ---	1-3,6, 17,18, 23,26, 47,59,60
X	DE 367 151 C (DR LADISLAUS) 18 January 1923 (1923-01-18) page 2, line 19 - line 111; claims 1-3,5; figure 1 page 3, line 1 - line 74 ---	1-3,5,6, 15,16, 29-31, 34,35, 47, 52-54,59
		-/-

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/04741

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 126 766 A (PROF. DR EMIL BAUR ET AL) 12 June 1919 (1919-06-12) page 2, line 32 - line 38; figure 1 -----	1-3,5,6, 15,16, 29,30, 34,35,59
X	CHEMICAL ABSTRACTS, vol. 85, no. 24, 13 December 1976 (1976-12-13) Columbus, Ohio, US; abstract no. 180031, WEAVER, ROBERT D. ET AL: "Direct use of coal in a fuel cell: feasibility investigation" XP002109767 abstract & U. S. NTIS, PB REP. (1975), PB-245917, 64 PP. AVAIL.: NTIS FROM: GOV. REP. ANNOUNCE. INDEX (U. S.) 1976, 76(2), 62 , 1975, -----	1-3,6, 14-16, 29-31, 47,59

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/04741

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